Chapter 2

HWF187, NY

Concentrations of Sulfur and Nitrogen Species and Cations

CASTNet measurements of sulfur and nitrogen air pollutants and cations were analyzed for the period 1990 through 2002. The data demonstrate a significant decline in SO_2 and sulfate concentrations. No trend is evident in the measurements of HNO_3, nitrate, and total nitrate. NH_4^+ concentrations were slightly lower. Cation measurements show two general patterns: relatively high Na^+ levels in coastal regions and relatively high Ca^{2+} in the agricultural Midwest. Cation-anion ratio data for 2002 show that anions were neutralized in a region of the United States roughly west of the Appalachian Mountains and were not neutralized in the East.

CASTNet filter packs were utilized during 2002 to measure concentrations of SO_2, SO_4^{2-}, HNO_3, NO_3^-, total nitrate (HNO_3 plus particulate NO_3^-), NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}. The presentation of the findings for each of the ten analytes includes a map of 2002 mean concentrations. The maps were prepared using concentration shading to illustrate the magnitude of concentrations for CASTNet sites in the continental United States. Maps of the 2002 quarterly mean concentrations are presented in Appendix B.

Additionally, analyses were prepared to determine any trend in concentration for each of the six primary pollutants using measurements from 34 eastern reference sites (Figure 1-1). The data from the 34 sites are presented via box plot values for each year for the period 1990 through 2002. The intersite variability among the 34 sites is shown graphically by the mean, median, and percentile values of annual concentrations for each year.

The subsection on cations includes maps of 2002 mean concentrations. An analysis of cations, anions, and cation-anion ratios is presented in this section.

Sulfur Species

Sulfur Dioxide

Figure 2-1 provides a map of 2002 mean SO_2 concentrations. The map shows a region of concentrations above 5.0 µg/m^3 extending from southwestern Kentucky and Illinois to western New York and New Jersey. This region corresponds to the major SO_2 source region shown in Figure 1-5. The highest annual SO_2

concentration levels were measured in and downwind of the Ohio River Valley with four sites showing concentrations above 10.0 µg/m^3. The single highest annual mean concentration (16.2 µg/m^3) measured at CASTNet sites in the continental United States was observed at QAK172, OH in eastern Ohio. Concentrations observed at western CASTNet sites were significantly lower than those measured in the East with only one site (OLY421, WA) measuring levels above 1.0 µg/m^3. The single highest SO_2 concentration (27.4 µg/m^3) measured for any CASTNet site was observed at HVT424, HI. The Kilauea Volcano produces the SO_2 concentrations measured in this national park.

Figure 2-2 provides a box plot that illustrates the trend in annual mean SO_2 concentrations over the 13-year period 1990 through 2002. The graph shows a sharp reduction in annual mean SO_2 concentrations in 1995 in response to the Phase I emission reductions, a small increase in the median value in 1997, and a significant decline since then. The difference between aggregated 3-year means from the beginning to the end of the 13-year period is 32 percent.

Particulate Sulfate

Annual mean particulate SO_4^{2-} concentrations observed during 2002 are presented in Figure 2-3. A narrow region with measured annual mean concentrations greater than 5.0 µg/m^3 extends from southern Indiana and Kentucky to western Pennsylvania. The peak concentration of 5.9 µg/m^3 was measured at MCK131, KY, a shift from QAK172, OH, which measured the highest sulfate level during 2001.

The SO_4^{2-} values measured at western sites ranged from 2.2 µg/m^3 at BBE401, TX to 0.4 µg/m^3 at LAV410, CA. Several western sites measured higher mean annual SO_4^{2-} concentrations than SO_2 concentrations. For example, the SO_4^{2-} concentrations at BBE401 and CHA467, AZ were 2.2 and 1.0 µg/m^3 versus SO_2 levels of 0.7 and 0.5 µg/m^3, respectively. The higher sulfate concentrations suggest that these sites received atmospheric sulfur from distant sources.

The trend in annual mean SO_4^{2-} concentrations is shown in the box plot in Figure 2-4. The plot shows a significant reduction in sulfate over the last 13 years. In particular, the difference between the aggregated 3-year means at the beginning and end of the 13-year period is 21 percent. This decline is less than the corresponding decline in SO_2 concentrations.

Nitrogen Species

Nitric Acid

A map of annual mean HNO_3 concentrations for 2002 is presented in Figure 2-5. A region in the eastern United States from western Kentucky to Connecticut observed fairly uniform concentrations that averaged about 2.0 µg/m^3. The highest annual mean concentration (3.0 µg/m^3) was measured in eastern Ohio (QAK172). JOT403, CA measured the highest concentration (2.9 µg/m^3) in California and the West.

The box plot shown in Figure 2-6 illustrates the trend in nitric acid concentrations. The figure indicates no significant trend over the 13 years.

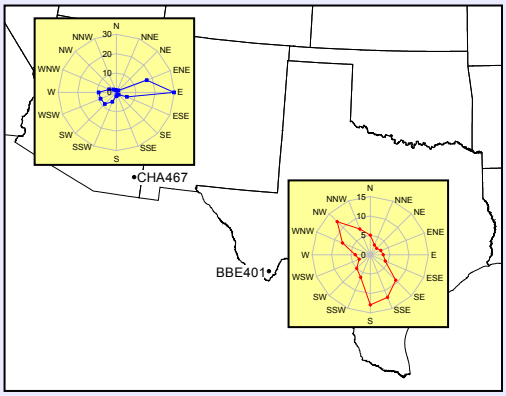
SO_2 and SO_4^{2-} Concentrations at Two Remote Southwestern Sites — Chiricahua National Monument and Big Bend National Park

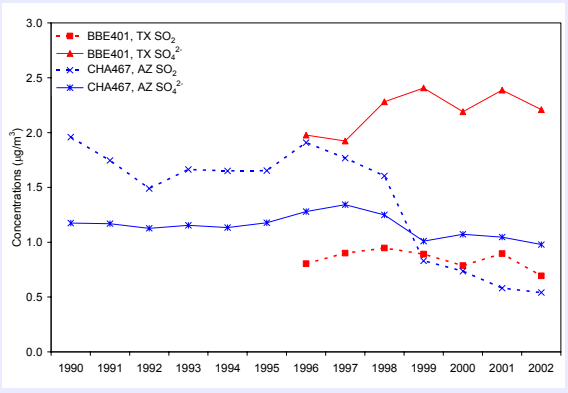
Trends in annual mean SO_2 and SO_4^{2-} concentrations measured at two southwestern CASTNet sites suggest that a significant contribution from long-range transport influences air quality at Chiricahua National Monument (CHA467) in Arizona and Big Bend National Park (BBE401) in west Texas. The measurements for CHA467 suggest SO_2 production from relatively nearby sources until 1999 when SO_4^{2-} concentrations began to exceed SO_2 levels. Mean annual SO_2 levels declined sharply over the period 1996 through 1999. SO_4^{2-} concentrations remained fairly steady with a slight decline over the two-year period 1998-1999. An interpretation of these results is that a nearby source of SO_2 was shut down around 1998 while SO_4^{2-} production was maintained through long-range transport of pollutants from distant sources. Furthermore, analysis of EPA data on SO_2 emission sources within 100 km of CHA467 indicates about an 89 percent reduction in SO_2 emissions from 1990 through 1996. SO_2 emissions in Arizona declined by an additional 38 percent over the period 1996 through 1999, including the elimination of emissions through the closing of a large copper smelter approximately 130 miles northwest (upwind) of CHA467.

The measurements from BBE401 show significantly higher SO_4^{2-} concentrations than SO_2 values over the period 1996 through 2002. SO_4^{2-} concentrations increased during 1998 and have stayed at approximately those levels. SO_2 concentrations stayed fairly constant over the entire period. The data strongly suggest the contribution of long-range transport to air quality at the national park.

The Big Bend Regional Aerosol and Visibility Observational Study (BRAVO) is a multiyear study of the causes of haze in the vicinity of BBE401. BRAVO is sponsored by EPA, NPS, and Texas Commission on Environmental Quality (TCEQ). Preliminary analyses from BRAVO (www2.nature.nps.gov/ard/bravo) indicate:

- "…most of the haze (at BBE401) was caused by sulfate aerosol with much less from the other aerosol species."
- "…the highest sulfate levels at Big Bend are associated with sources along the U.S.-Mexico Border, and to the north and east of Big Bend, including those in Texas and the Eastern U.S."





Particulate Nitrate

Figure 2-7 presents 2002 annual mean concentrations of particulate nitrate. The map depicts a narrow region of relatively high levels (i.e., 2.0 µg/m^3 or greater) from Illinois northeastward to Ontario, Canada. The single highest value (3.9 µg/m^3) was observed in northern Illinois at STK138. The intersite variability in the concentrations that were observed at the eastern sites is significant. For example, annual mean concentrations measured in Pennsylvania varied from 0.4 to 1.4 µg/m^3. While most western sites measured annual mean concentrations of 0.5 µg/m^3 or lower, three sites in southern California measured values above 1.0 µg/m^3. SEK402, CA measured the highest value (1.7 µg/m^3) in the West.

The box plot in Figure 2-8 illustrates the trend in annual mean particulate nitrate concentrations. The data, while showing no overall trend, show a decline for 2002.

Total Nitrate

Annual mean concentrations of total nitrate for 2002 are shown in Figure 2-9. The map displays a region in the eastern United States with concentrations above 4.0 µg/m^3 extending from Illinois across Indiana to Ohio. The highest annual mean concentration (5.2 µg/m^3) was observed at SAL133, IN. Western CASTNet sites in southern California also measured relatively high concentrations with JOT403 having the highest value (4.1 µg/m^3). Figure 2-10 provides the box plot for total nitrate values. The plot indicates no trend.

Particulate Ammonium

Figure 2-11 presents a map of 2002 annual mean particulate NH_4^+ concentrations. Sites in Illinois, Indiana, northern Kentucky, and Ohio, observed concentrations greater than or equal to 2.0 µg/m^3. With the exception of sites in Minnesota, northern New England, North Carolina, and Florida, most eastern sites measured levels above 1.0 µg/m^3. Most western sites (all but four) observed annual mean NH_4^+ concentrations below 0.5 µg/m^3.

Figure 2-12 presents a box plot of annual mean NH_4^+ concentrations. The data show a slight reduction in annual mean NH_4^+ concentrations over the 13-year period.

Cations

Annual mean concentrations of Na^+, K^+, Mg^{2+}, and Ca^{2+} for 2002 are shown in Figures 2-13 through 2-16. The geographic patterns observed for 2002 are similar to those observed for 2001 and 2000. Figure 2-13 shows that the highest annual mean Na^+ concentrations were observed along the eastern coastal plain. Levels above 1.00 µg/m^3 were observed from the Everglades (EVE419) in Florida to BFT142, NC. A single value above 0.50 µg/m^3 was observed on the West Coast at PIN414, CA. Concentrations above 0.20 µg/m^3 were measured along both coasts. The highest annual mean Na^+ concentration (2.91 µg/m^3) in the network was measured at Virgin Islands National Park (VII423). Figures 2-14 and 2-15 show relatively low annual mean K^+ and Mg^{2+} measured concentrations and no discernible patterns. As shown in Figure 2-16, the highest annual mean Ca^{2+}

concentrations were observed in the Great Plains and agricultural Midwest, extending from Kansas to Ontario, Canada. Relatively high levels were also measured along the East Coast from EVE419, FL to BFT142, NC. An annual mean concentration of 0.54 µg/m^3 was observed at BBE401, TX and 0.51 µg/m^3 at MEV405, CO.

The primary use of the cation measurements is to gauge the acidity (anion-cation balance) of the air quality as measured by the filter packs at all CASTNet sites. Although CASTNet measures both anions and cations, it was not designed to measure every ion that contributes to aerosol acidity, e.g., carbonate, chloride and phosphate. Figure 2-17 shows annual mean ratios of cations (NH_4^+, Ca^{2+}, K^+, and Mg^{2+}) to anions (SO_4^{2-} and NO_3^-) throughout the United States. Na^+ values were excluded from the analysis because Cl^- was not measured. Na^+ and Cl^- coexist as NaCl. The map shows a dividing line between ratios greater than 1.00 and less than 1.00 was measured roughly along the Appalachian Mountain chain from Alabama to Maine. Evidently, agricultural activities in the Midwest and generally dusty conditions in the West produced surplus cations, which neutralized the acidic particles on the CASTNET filters. Air quality east of the Appalachians is dominated by acidic particles. Ratios along both the East and West coasts were less than 1.00.

The cation measurements suggest two geographic patterns. First, the highest annual mean Na^+ concentrations were in or near costal regions from Florida to North Carolina and in California and Washington. Second, the highest annual mean Ca^{2+} concentrations were measured in the Great Plains and agricultural Midwest. No patterns were observed for K^+ and Mg^{2+}.

Figure 2-18 presents a time series of the cation-anion ratios at four sites over the period January through December 2002. The agricultural sites at STK138, IL and SPD111, TN measured quarterly ratios above 1.0. The ratios measured at LRL117, PA were generally less than 1.0 although the values were near 1.0 during the last three quarters. The ratios measured at the forested, complex terrain site at LYE145, VT were near 1.0. Evidently, the acidic aerosols were almost completely neutralized at this sensitive ecosystem.

Figure 2-19 provides a time series of quarterly mean cation-anion ratios aggregated over the 34 reference sites. Cation and anion concentrations in micro equivalents per liter (µeq/l) are also provided. The aggregated ratio values equaled or exceeded 1.0 during 9 of the 12 quarters. No trend is evident in this time series.

Figure 2-1. Annual Mean SO_2 Concentrations ($\mu g/m^3$) for 2002

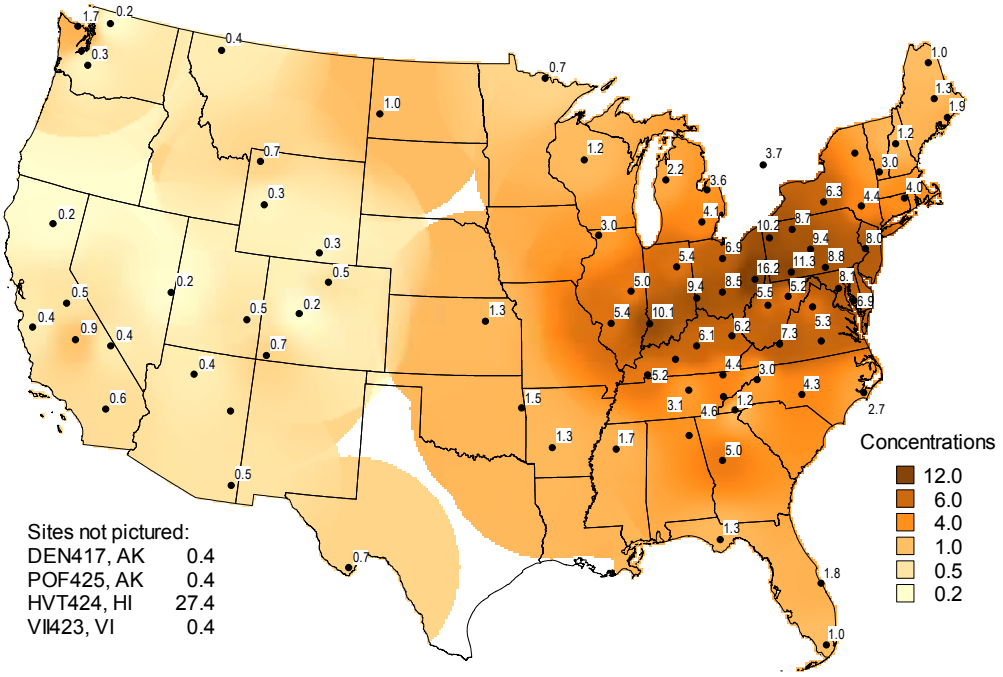


Figure 2-2. Trend in Annual SO_2 Concentrations ($\mu g/m^3$) — Eastern United States

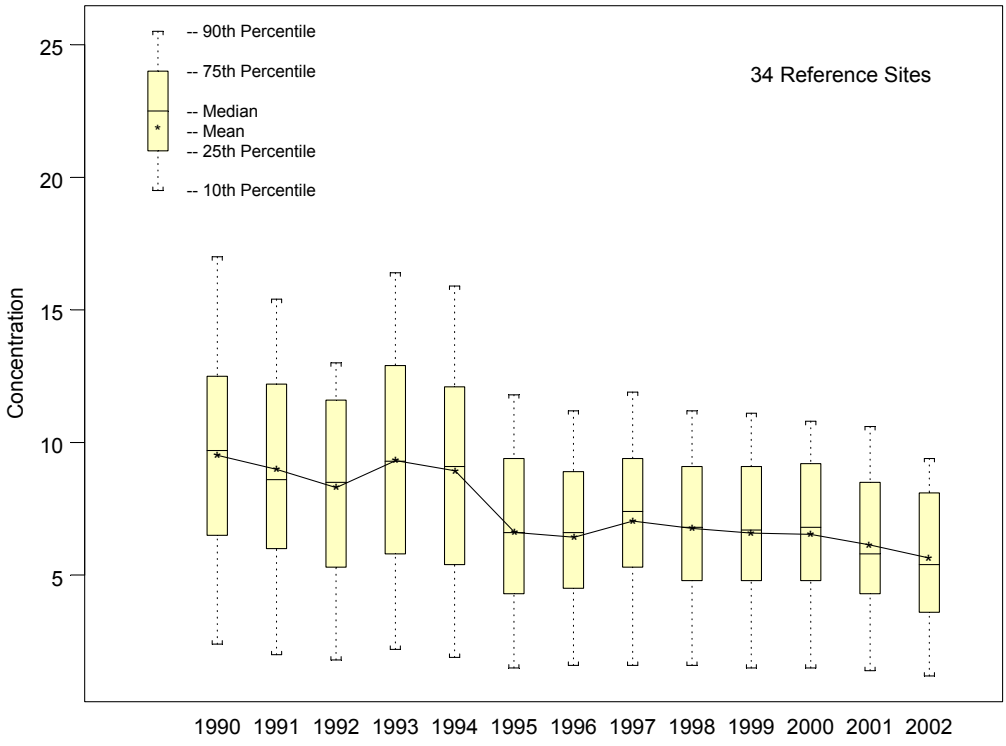


Figure 2-3. Annual Mean SO_4^{2-} Concentrations (µg/m^3) for 2002

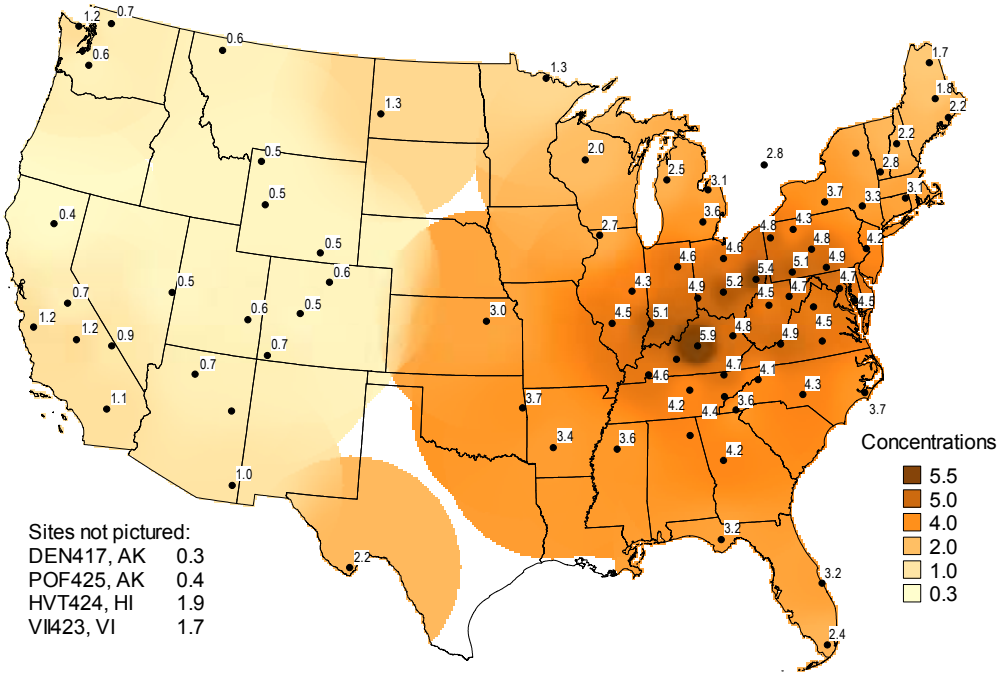


Figure 2-4. Trend in Annual SO_4^{2-} Concentrations (µg/m^3) — Eastern United States

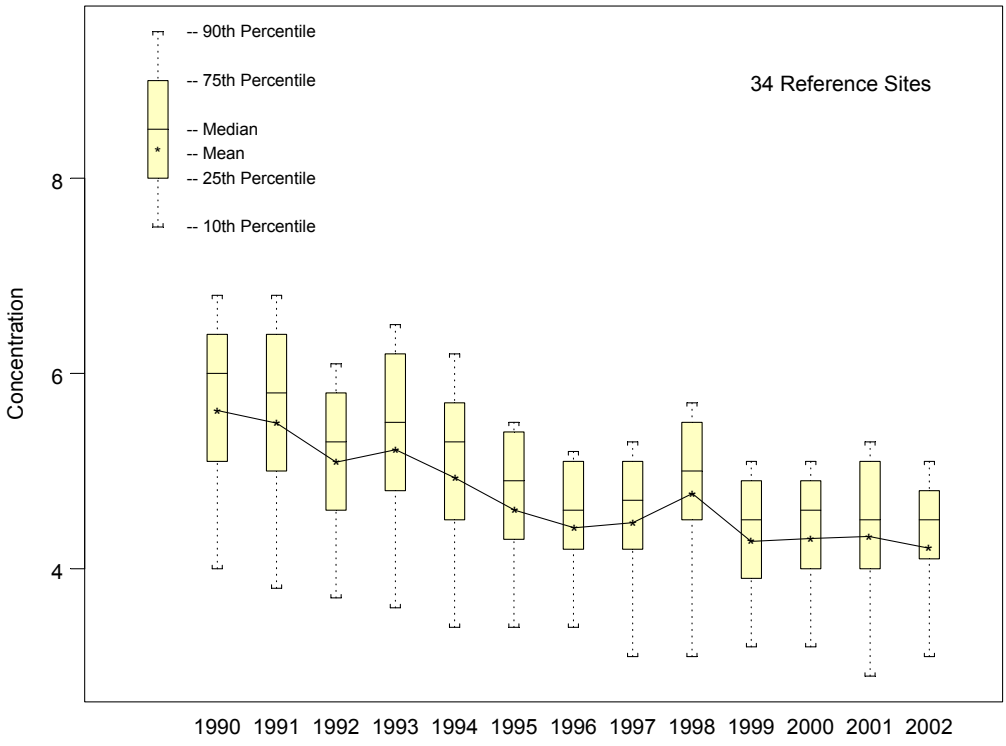


Figure 2-5. Annual Mean HNO_3 Concentrations ($\mu g/m^3$) for 2002

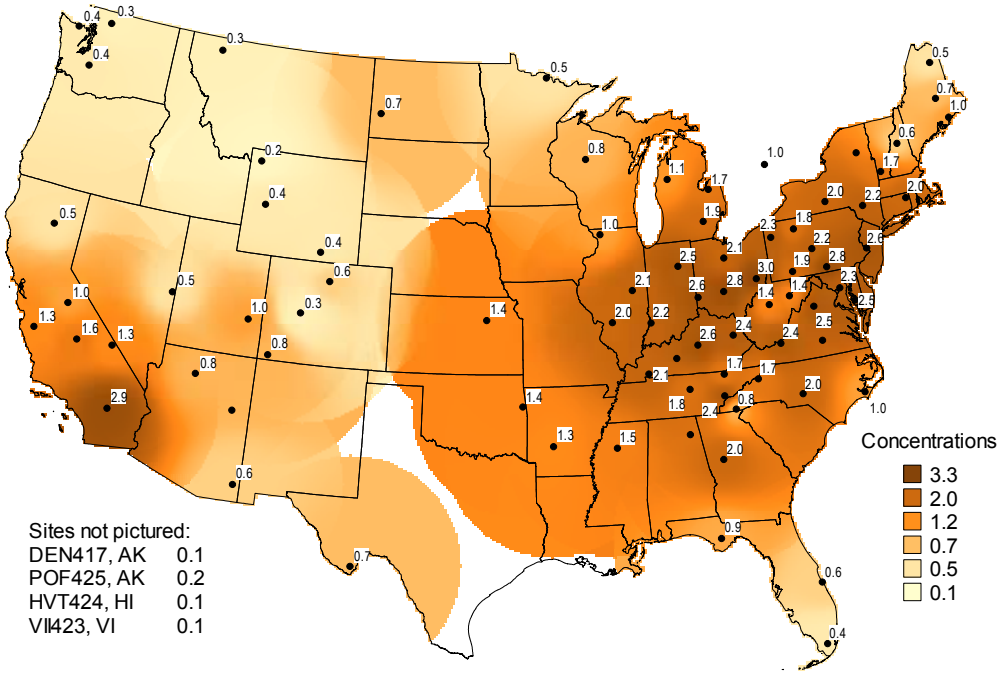


Figure 2-6. Trend in Annual HNO_3 Concentrations ($\mu g/m^3$) — Eastern United States

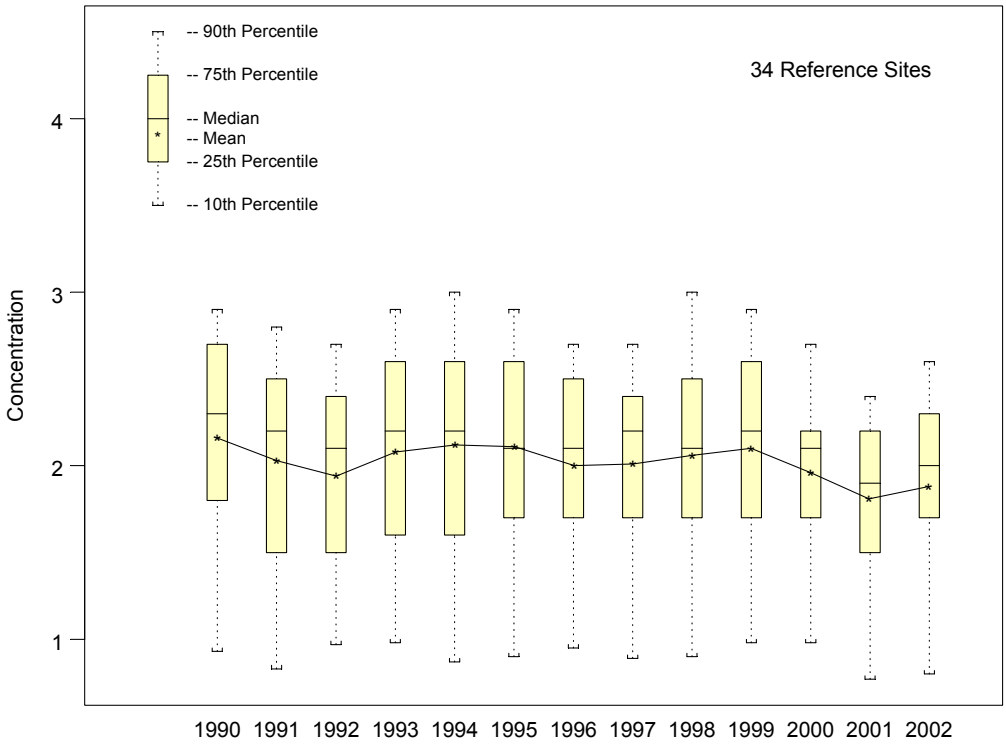


Figure 2-7. Annual Mean NO_3^- Concentrations ($\mu g/m^3$) for 2002

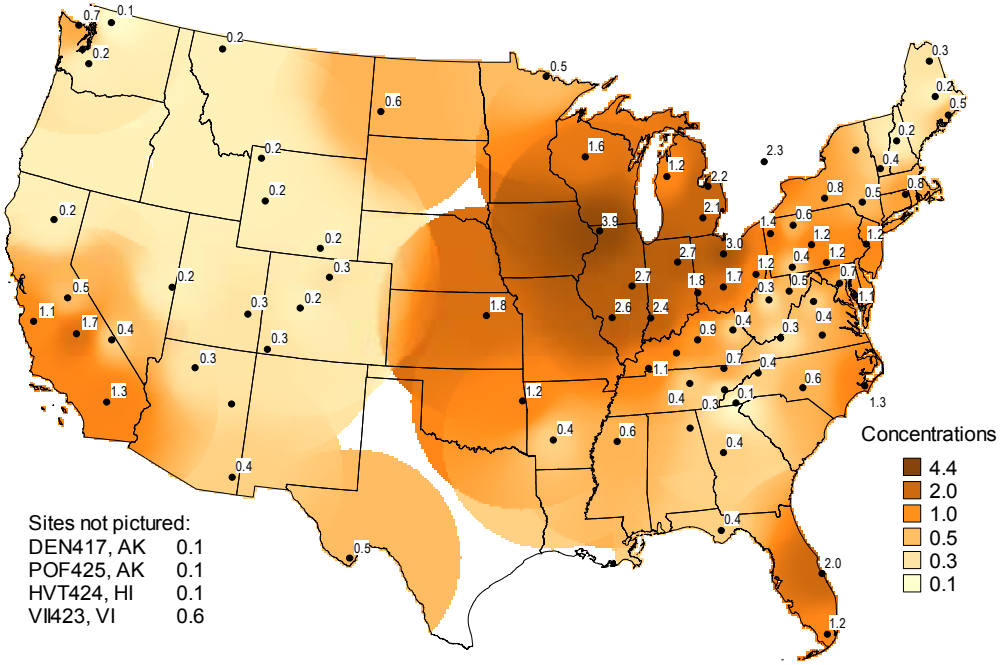


Figure 2-8. Trend in Annual NO_3^- Concentrations ($\mu g/m^3$) — Eastern United States

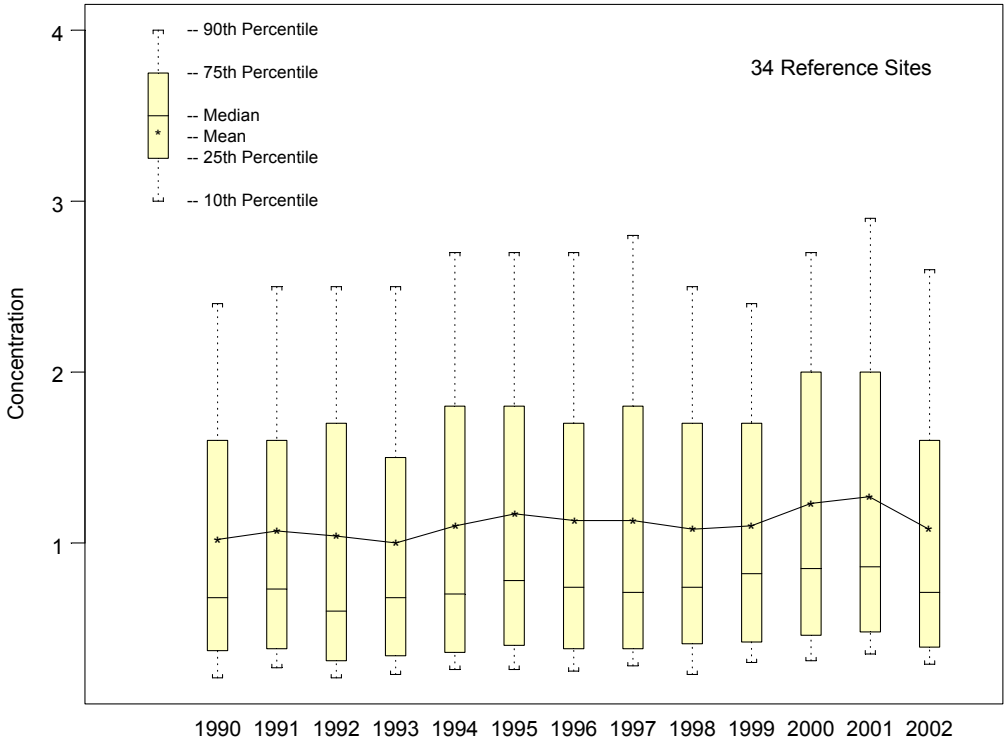


Figure 2-9. Annual Mean Total NO_3^- Concentrations ($\mu g/m^3$) for 2002

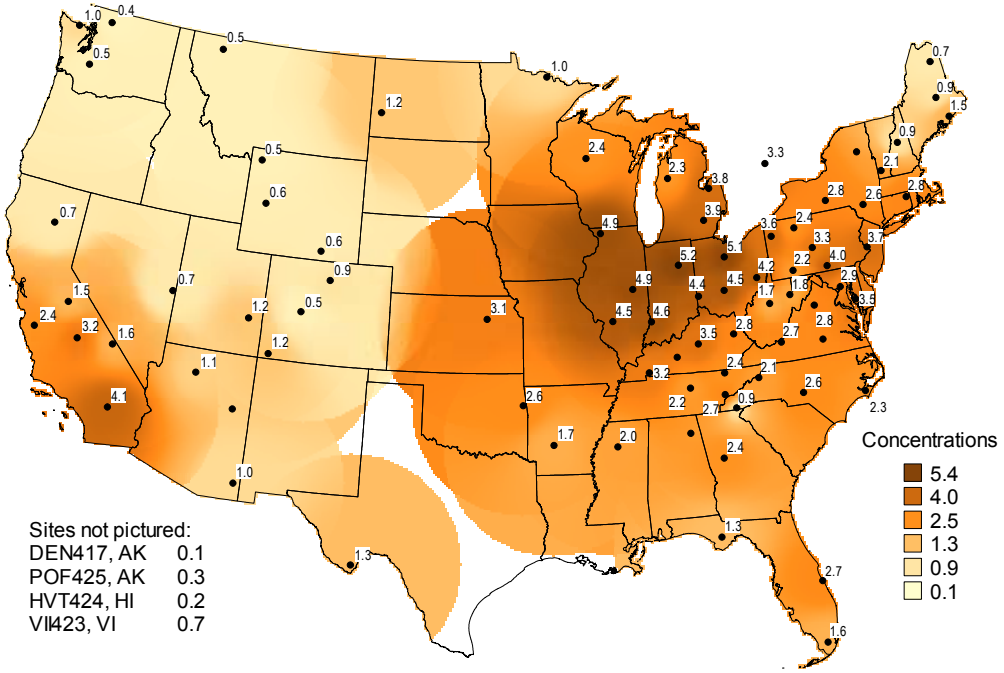


Figure 2-10. Trend in Annual Total NO_3^- Concentrations ($\mu g/m^3$) — Eastern United States

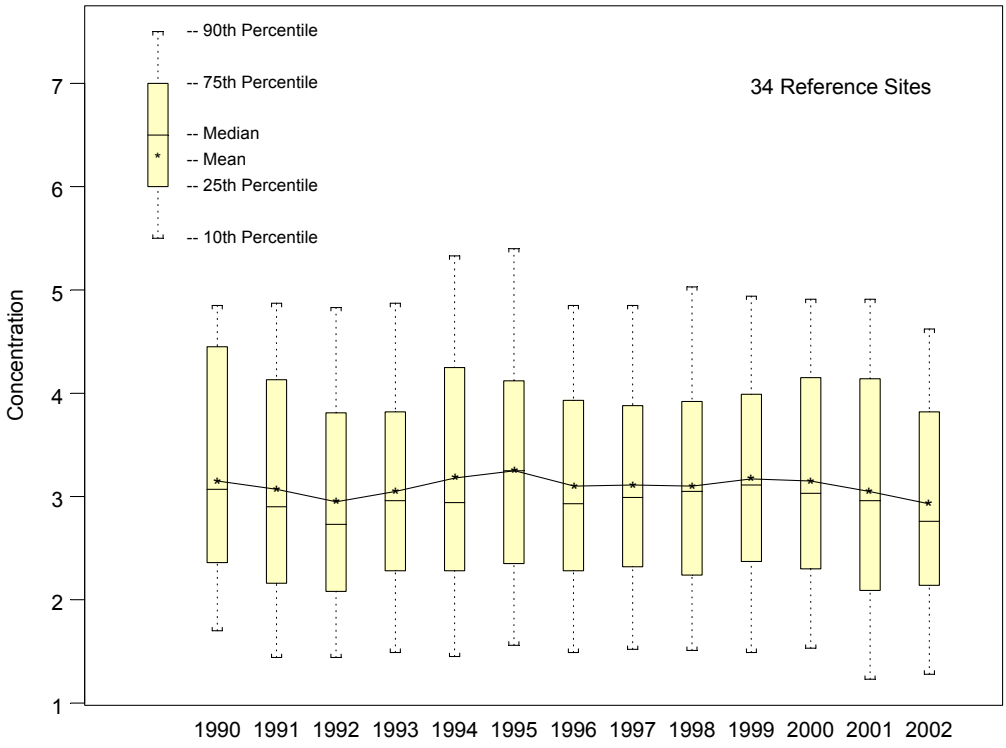


Figure 2-11. Annual Mean NH_4^+ Concentrations (μg/m^3) for 2002

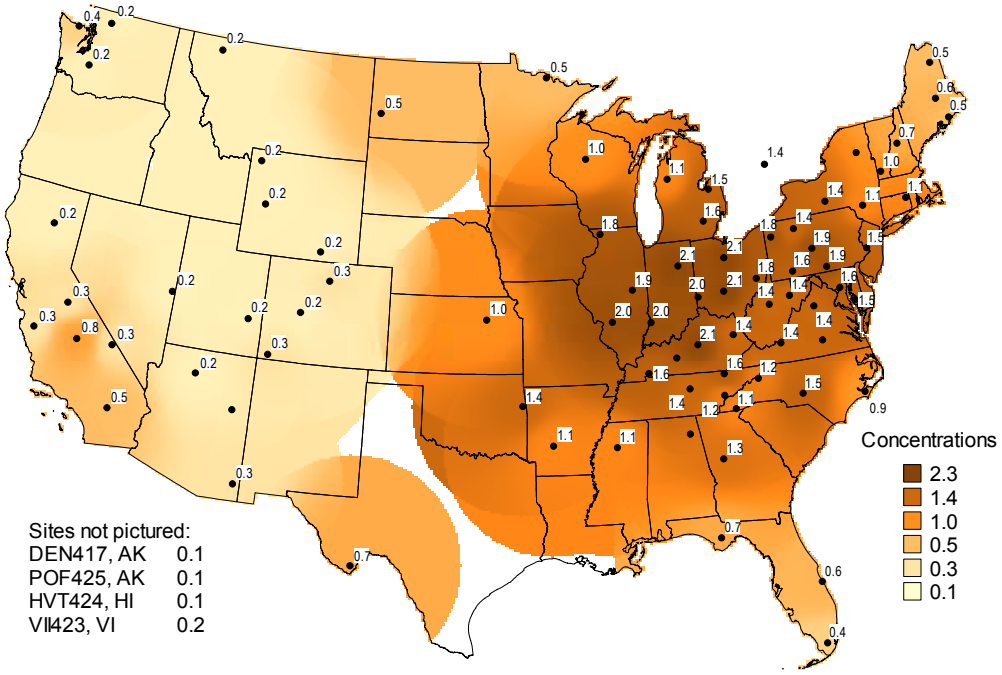


Figure 2-12. Trend in Annual NH_4^+ Concentrations (μg/m^3) — Eastern United States

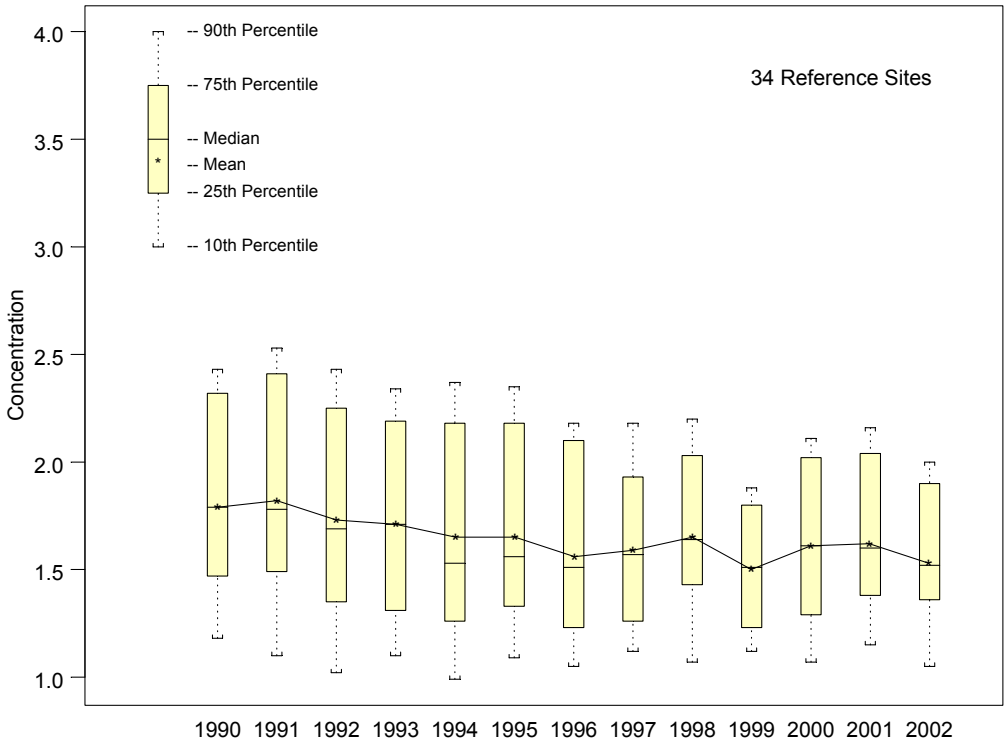


Figure 2-13. Annual Mean Na^+ Concentrations ($\mu g/m^3$) for 2002

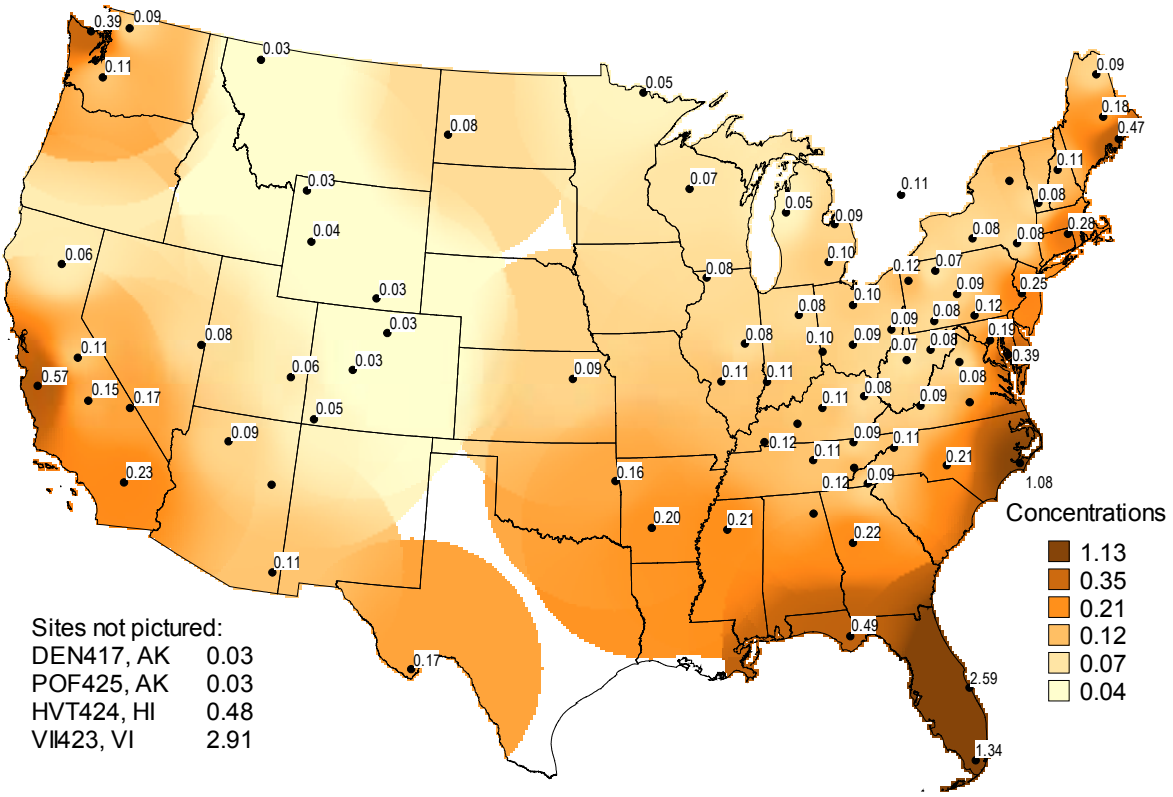


Figure 2-14. Annual Mean K^+ Concentrations ($\mu g/m^3$) for 2002

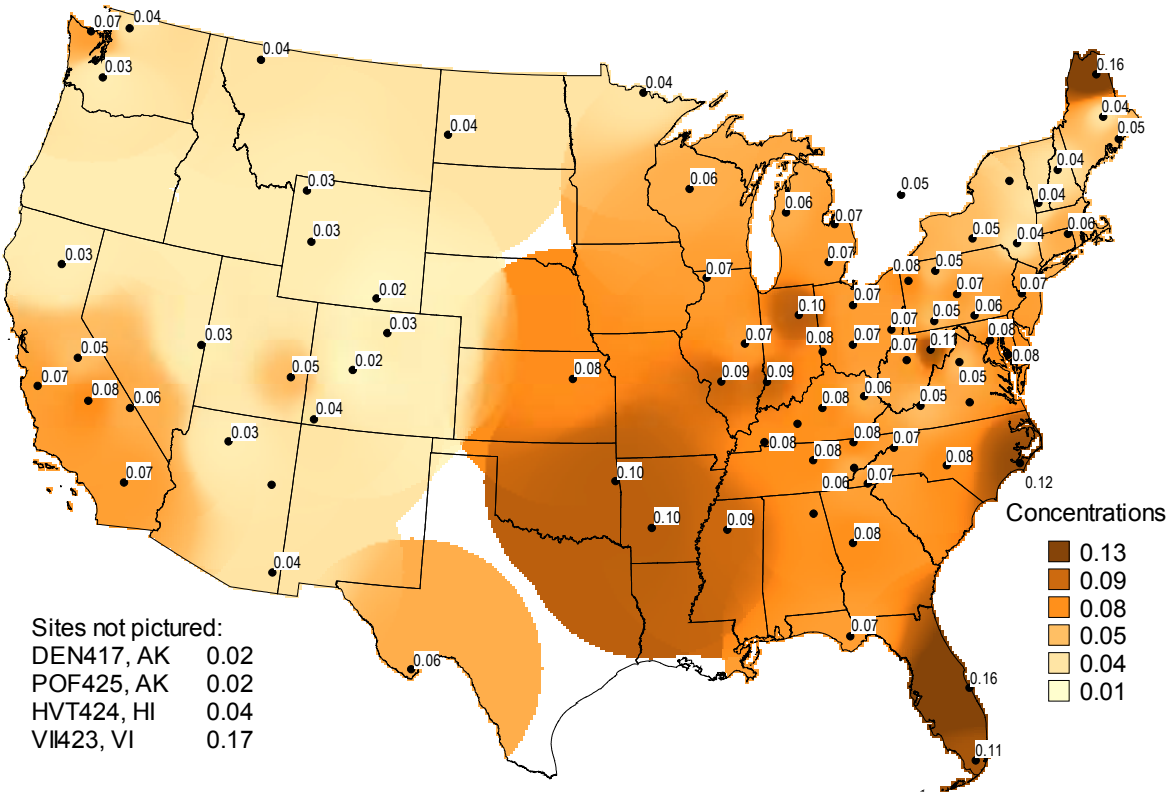


Figure 2-15. Annual Mean Mg^{2+} Concentrations ($\mu g/m^3$) for 2002

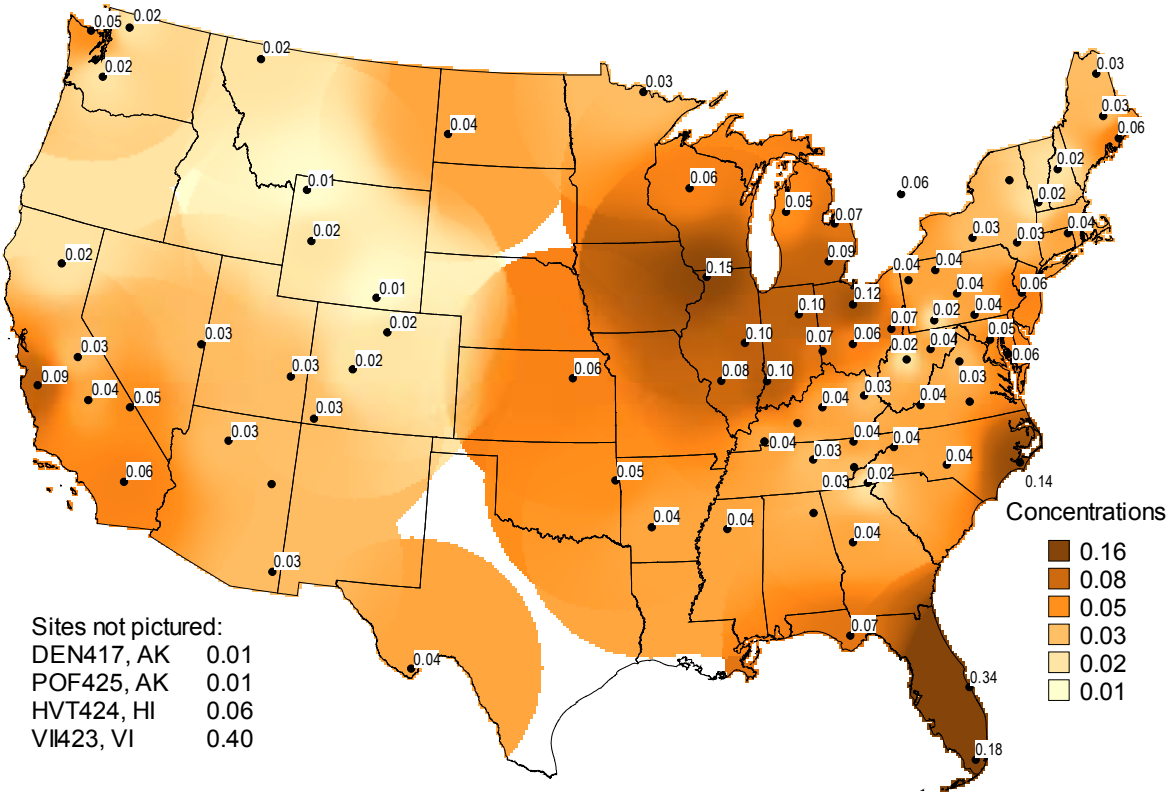


Figure 2-16. Annual Mean Ca^{2+} Concentrations ($\mu g/m^3$) for 2002

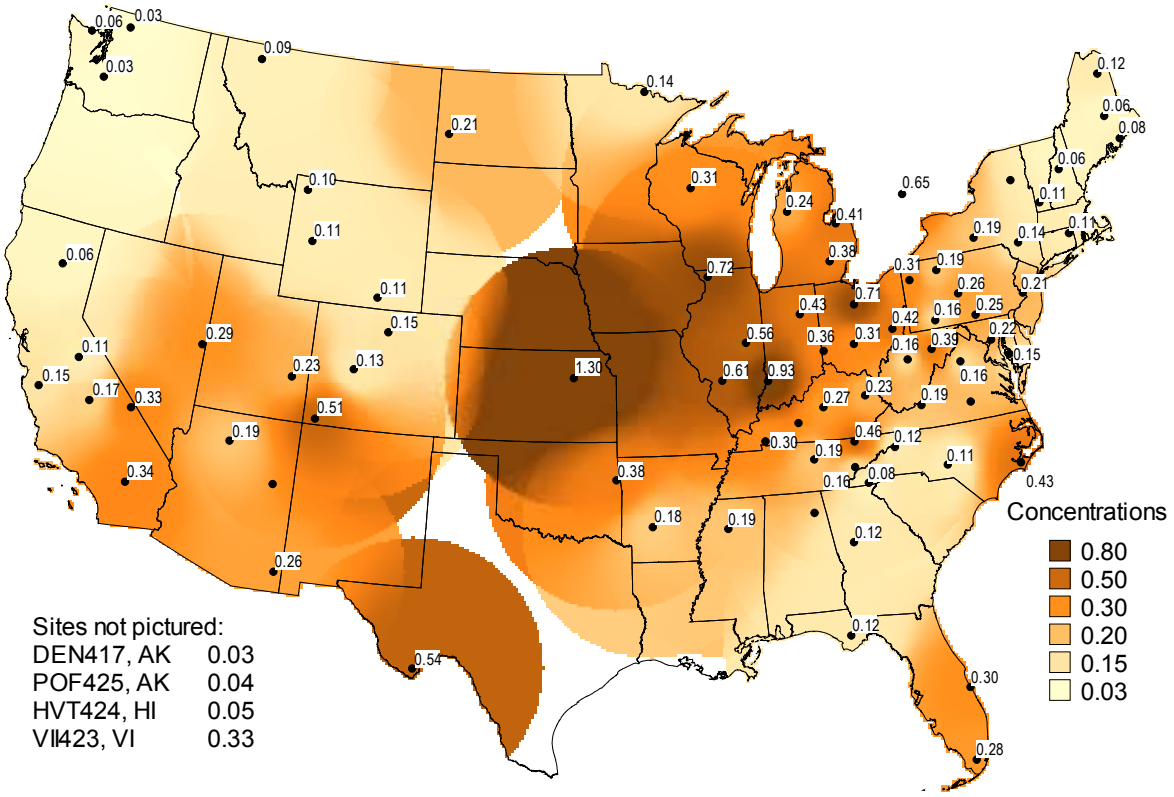


Figure 2-17. Annual Mean Cation-Anion Ratios for 2002

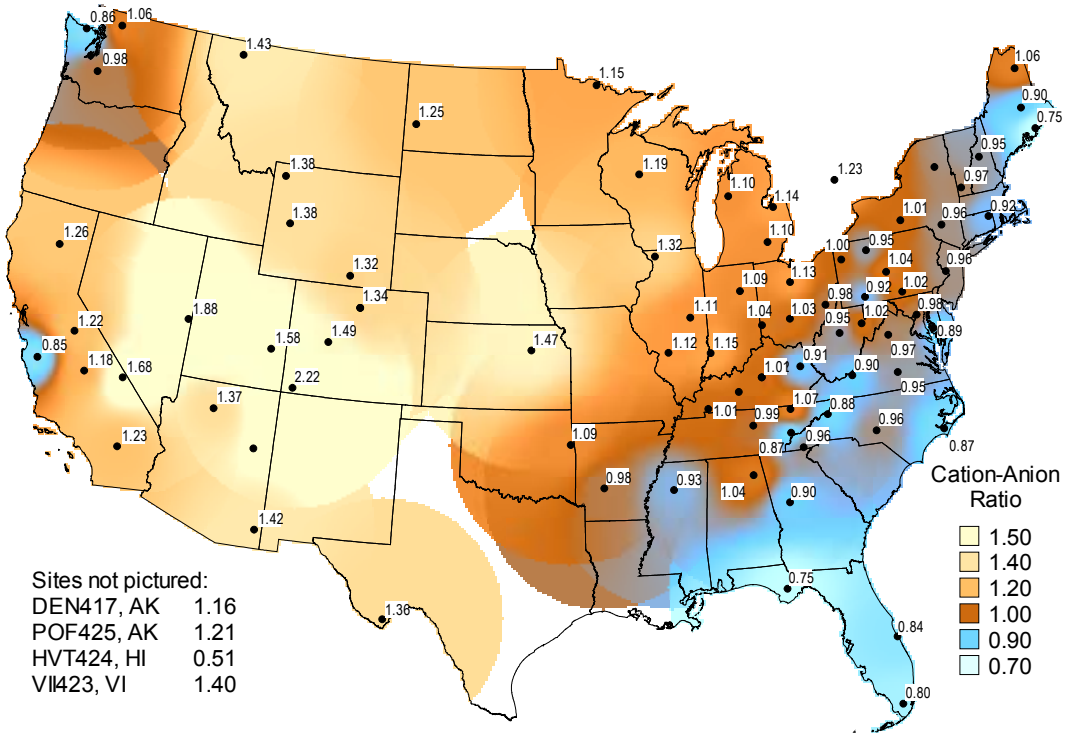


Figure 2-18. Time Series of Cation-Anion Ratios

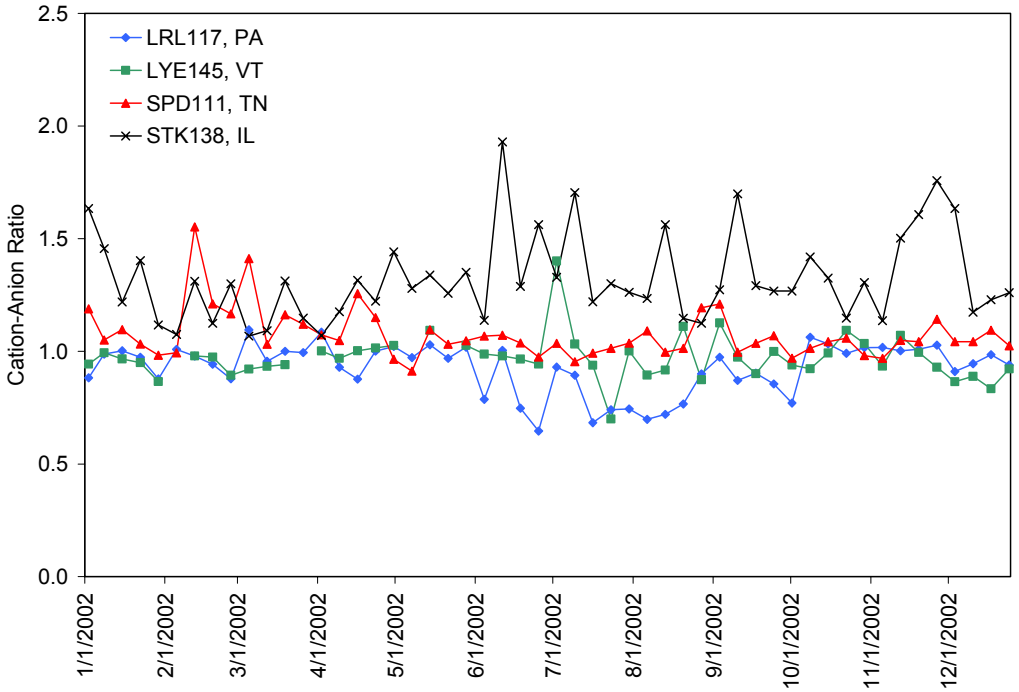
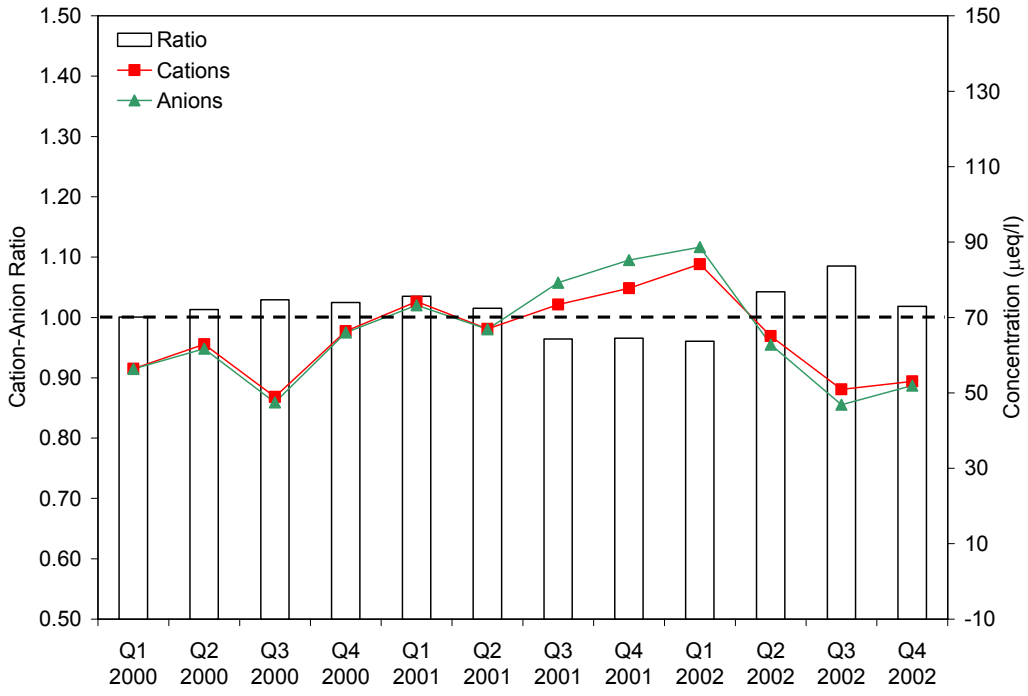


Figure 2-19. Trend in Quarterly Mean Cation and Anion Concentrations (µeq/l) and Ratios (Eastern Reference Sites)



CASTNet and IMPROVE Sulfate Data

CASTNet and IMPROVE are both long-term air-monitoring networks with sites spanning the United States. Although sampling protocols and filter media differ, both networks collect sulfate samples. CASTNet collects weekly SO_4^{2-} samples while IMPROVE collects 24-hour samples every three days. CASTNet operated 84 sites and IMPROVE operated 156 sites during 2002. Collocated CASTNet-IMPROVE sampling systems were operated at 35 sites. If combined, a CASTNet-IMPROVE database containing data from over 200 sites would provide extensive information on the status of sulfate concentrations across the United States. The comparability of the two databases was investigated by:

(1) analyzing quarterly mean concentrations collected at six collocated sites (three eastern and three western),
(2) plotting time series of weekly and 24-hour concentrations for the six sites, and
(3) evaluating the statistical relationships between the two sets of quarterly means.

Figure 2-i shows time series of quarterly and annual mean concentrations for three collocated eastern sites, which are located at Everglades National Park, FL (Everglades); Great Smoky Mountains National Park, TN (Smoky Mountains); and Shenandoah National Park, VA (Shenandoah). The Everglades site quarterly data show that the CASTNet results were slightly higher than IMPROVE. For 2002, the annual mean IMPROVE SO_4^{2-} concentration at the Shenandoah site was higher than the CASTNet level. The concentrations presented for the Everglades and Smoky Mountains sites are from 1999 through 2002. The concentrations presented for the Shenandoah site cover the period 1990 through 2002. Time series of weekly (CASTNet) and 24-hour (IMPROVE) concentrations for the same three sites are presented in Figure 2-ii. Overall, the two figures show strong qualitative agreement between the two databases.

Time series of quarterly mean concentrations for the three collocated western sites (Yellowstone National Park, WY; Mt. Rainier National Park, WA; and Pinnacles National Park, CA) are given in Figure 2-iii. Figure 2-iv illustrates weekly and 24-hour concentrations for the same three sites. Again, the qualitative agreement between the two databases is strong, with the exception of the last two quarters of 2002 at the Washington site. The CASTNet measurements for the California site (PIN414) are somewhat higher than the corresponding IMPROVE values.

Figure 2-v provides a scatter diagram of quarterly mean SO_4^{2-} values for all six sites combined over the period 1999 through 2002. The data show a strong correlation ($R^2 = 0.9665$) over a concentration range from near zero to 9.0 $\mu g/m^3$. The regression line, however, shows that the CASTNet measurements are slightly higher than the IMPROVE measurements. Because of the good agreement, the CASTNet and IMPROVE SO_4^{2-} data were combined to produce a map (Figure 2-vi) of annual mean SO_4^{2-} concentrations. The map shows the highest SO_4^{2-} levels were centered on the Ohio Valley. The western data show that relatively high concentrations were measured along the southern tier of the network – from southern California to BBE401, TX.

Figure 2-i. Eastern Sites – Quarterly and Annual Mean SO_4^{2-} Concentrations ($\mu g/m^3$)

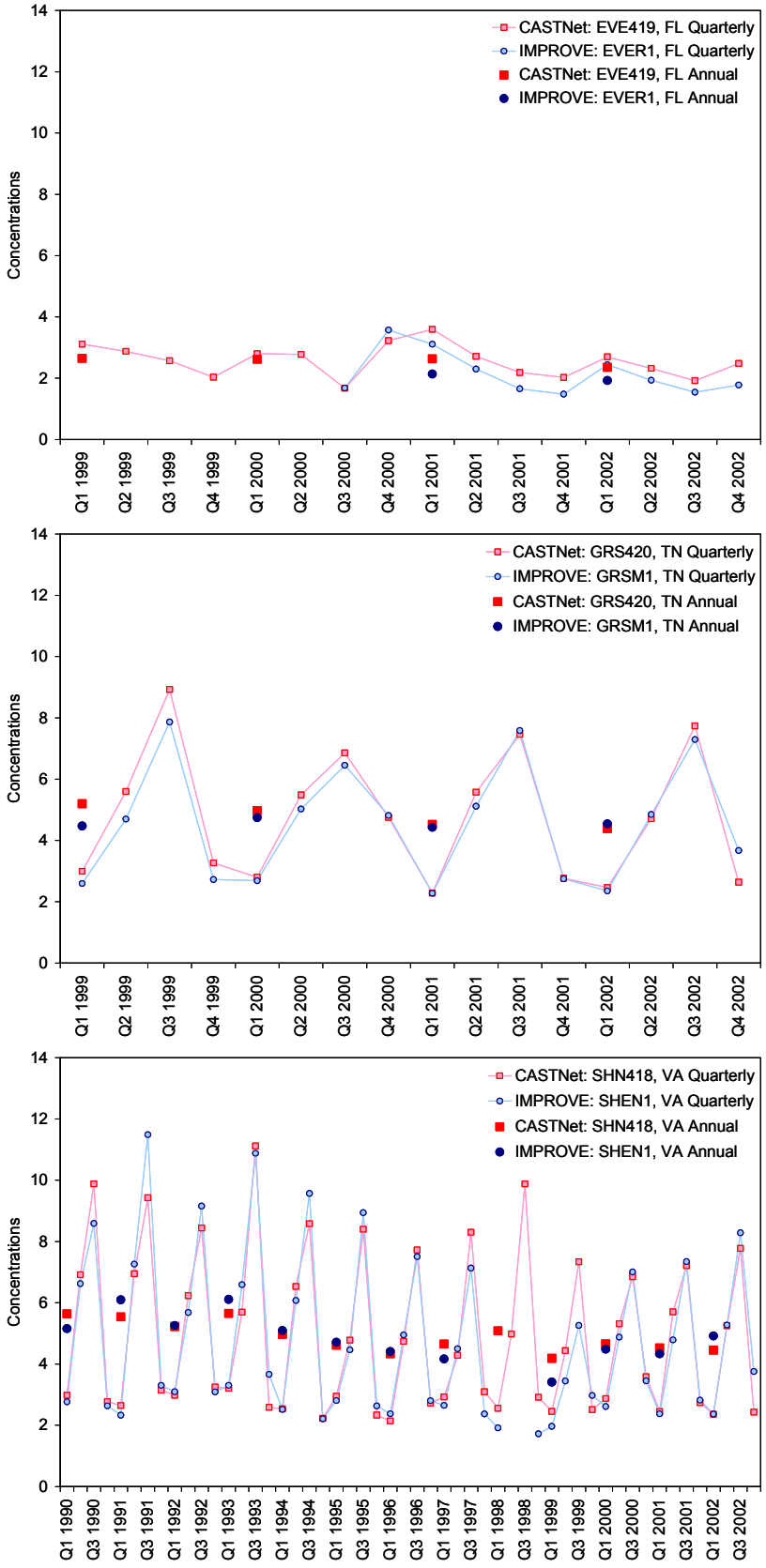


Figure 2-ii. Eastern Sites – Time Series of Weekly and 24-Hour SO_4^{2-} Concentrations ($\mu g/m^3$) (2001-2002)

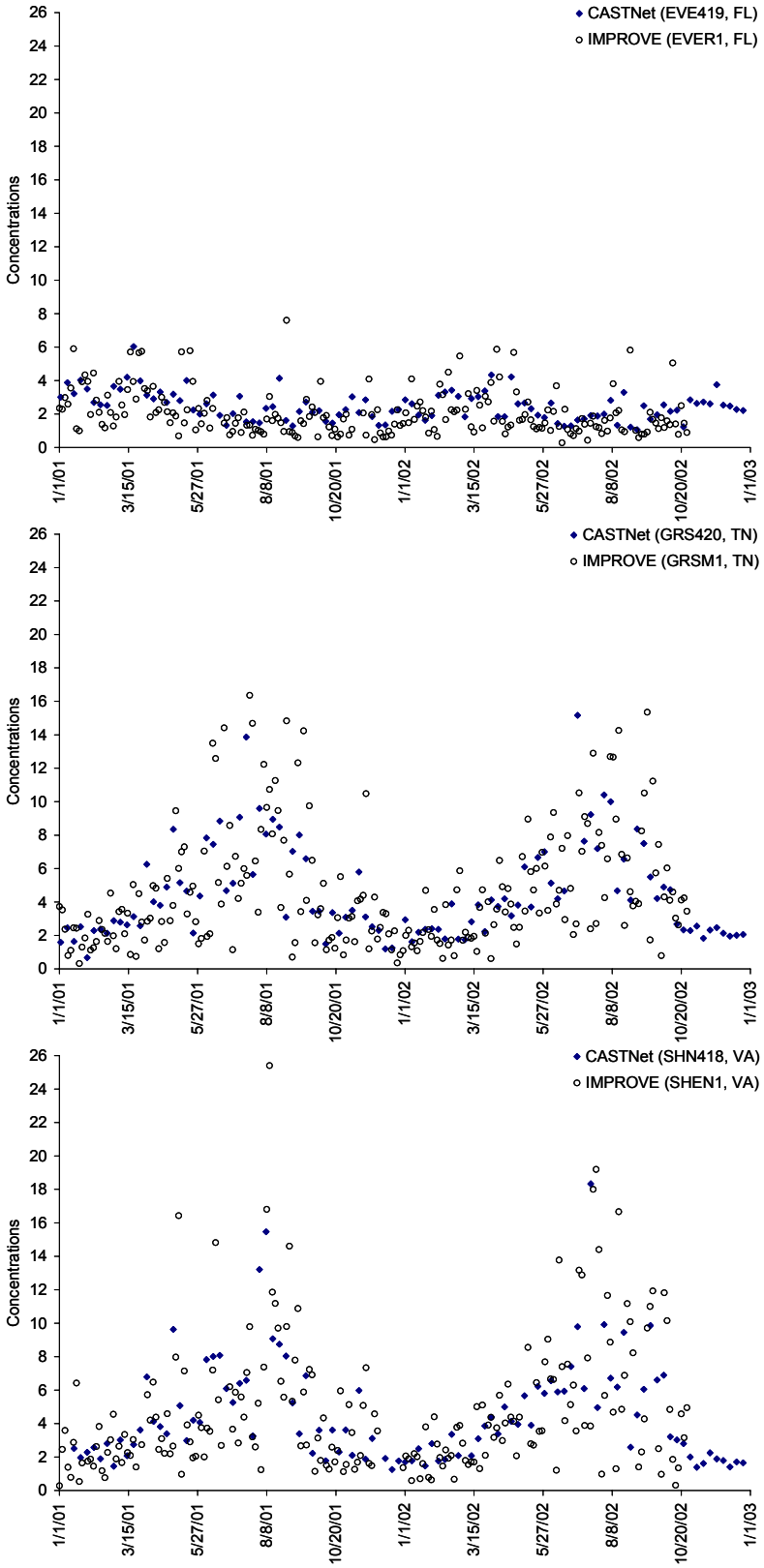


Figure 2-iii. Western Sites – Quarterly and Annual Mean SO_4^{2-} Concentrations ($\mu g/m^3$) (1996-2002)

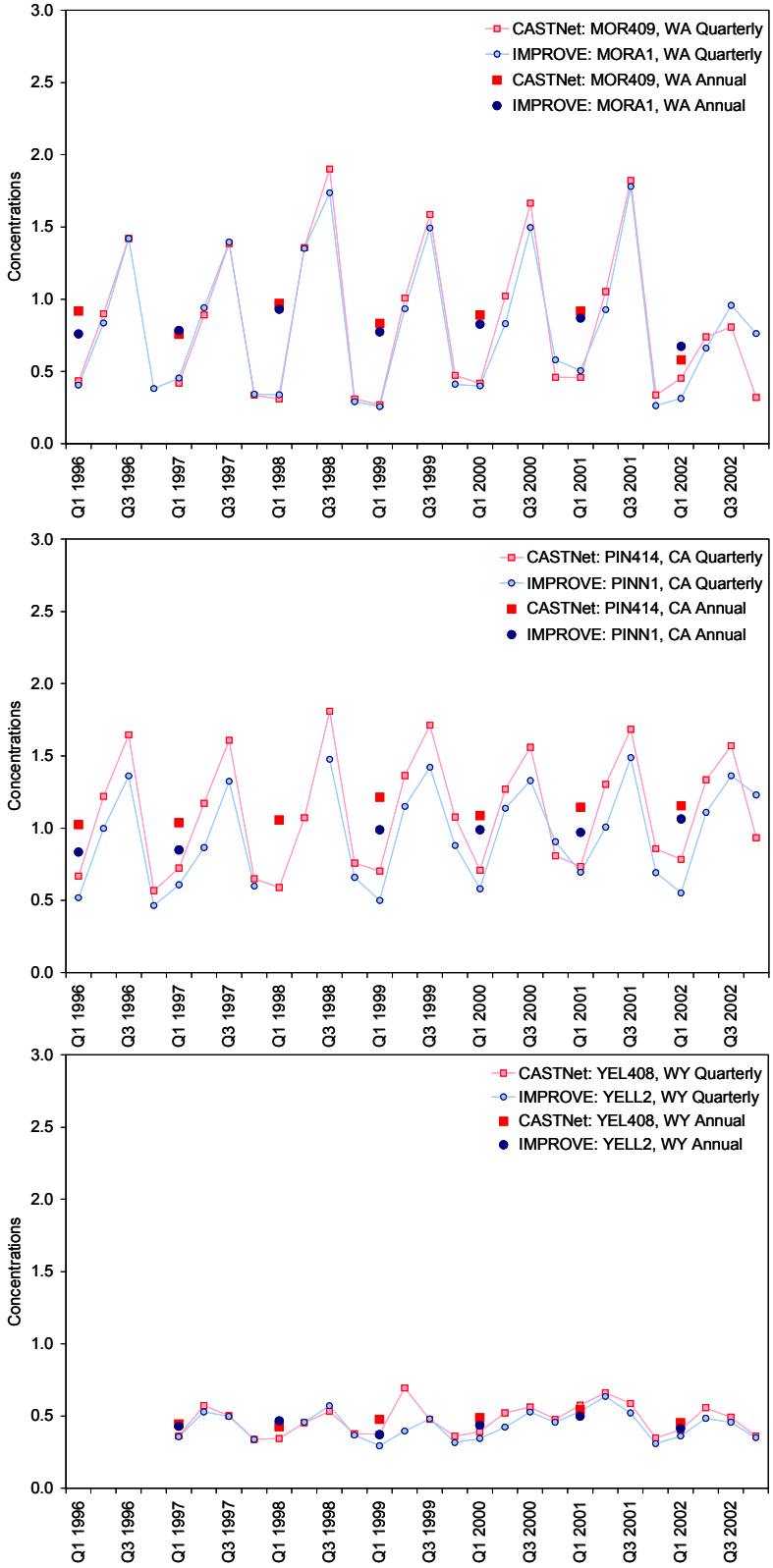


Figure 2-iv. Western Sites – Time Series of Weekly and 24-Hour SO_4^{2-} Concentrations ($\mu g/m^3$) (2001-2002)

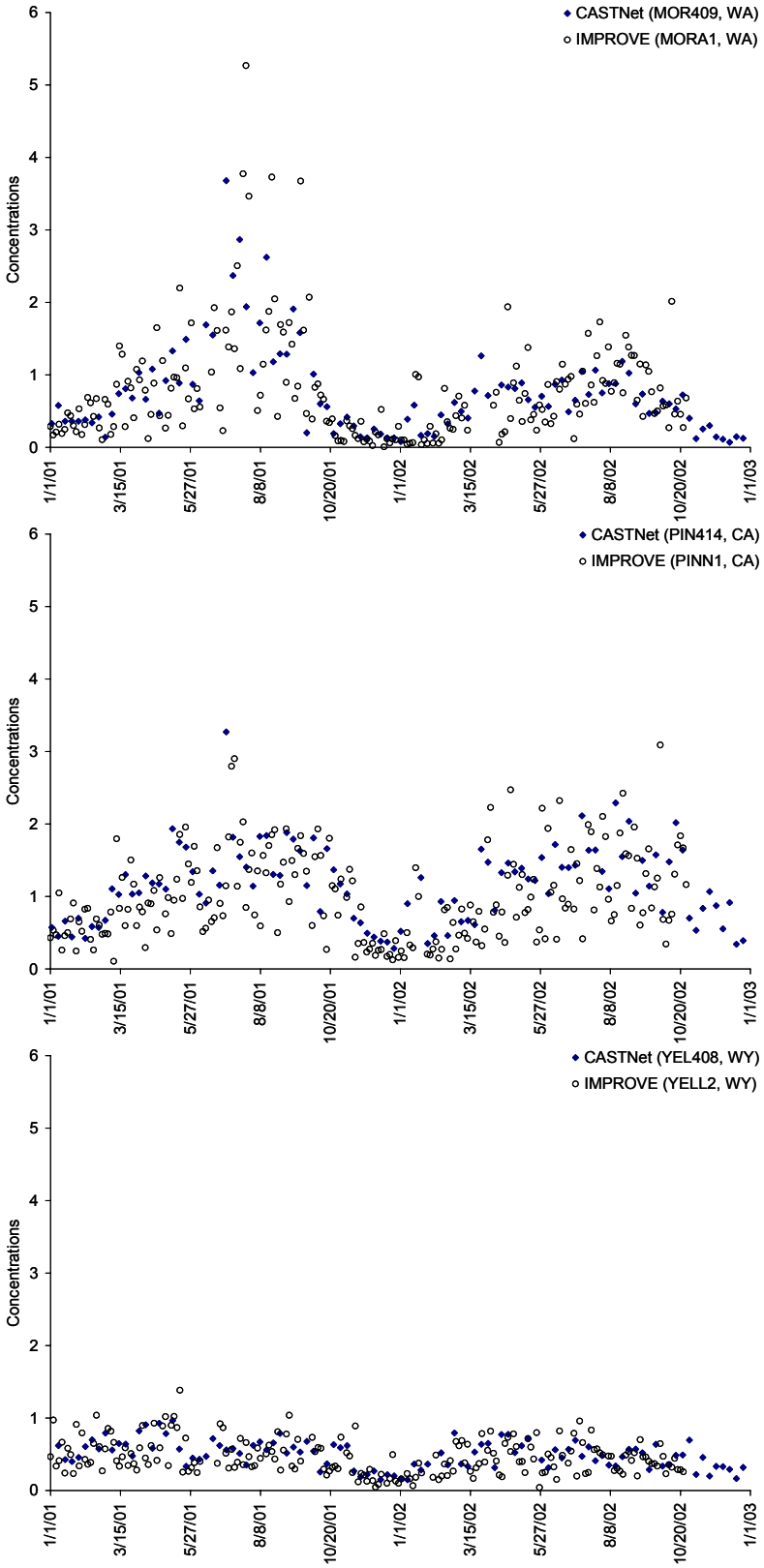


Figure 2-v. Scattergram of CASTNet and IMPROVE SO_4^{2-} Concentrations ($\mu g/m^3$) for 1999 through 2002

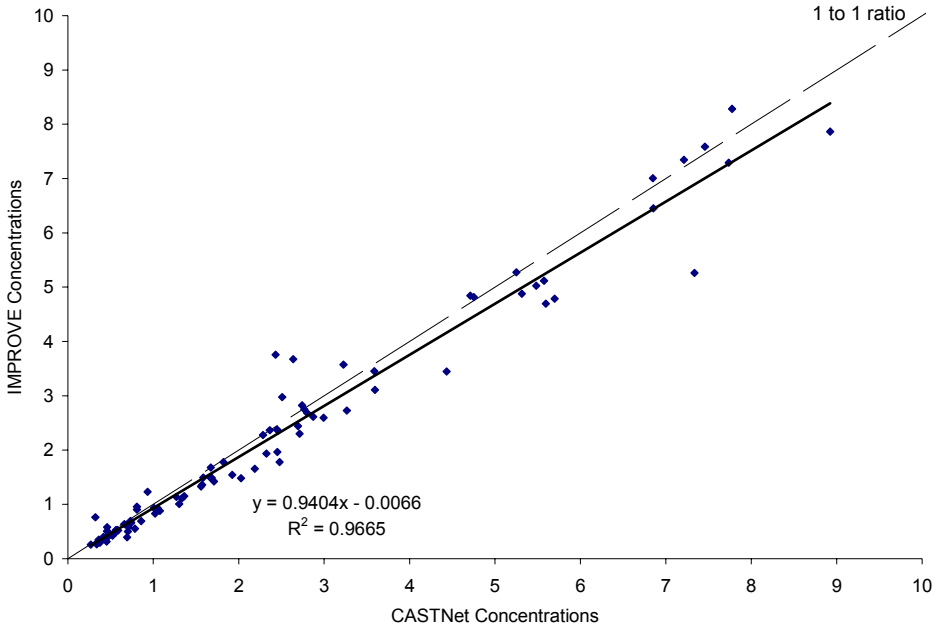


Figure 2-vi. Map of CASTNet and IMPROVE SO_4^{2-} Concentrations ($\mu g/m^3$) for 2002